

Determination of Boron Coordination in Nuclear Waste Form Glasses by Soft X-Ray Synchrotron Radiation and Nuclear Magnetic Resonance Techniques

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INTRODUCTION

A multitude of individual components comprising borosilicate nuclear waste glasses are currently being investigated using x-ray absorption fine structure (XAFS) and nuclear magnetic resonance (NMR) techniques along with a host of other characterization methods. The focus of boron studies in glasses is to determine the amount of three- versus four-coordinate boron, the latter of which is generally accepted as being obtained through association with alkali ions. Structural characterization of boron is of particular importance as the knowledge of the interactions between B, O, Na, and other species is essential for building a fundamental understanding of glass durability.¹ One accepted method to obtain local structural information about boron is via ¹¹B NMR. Boron coordinated to three oxygens in a trigonal planar configuration gives rise to an asymmetric electric field gradient and a characteristic NMR line shape which is significantly different from tetrahedral four-coordinate B. NEXAFS spectroscopy of the B K edge has been well-characterized and the distinctive π^* electronic feature characteristic of B sp^2 hybridization arising from a trigonal planar environment provides a signature of three-coordinate boron. NMR requires specially formulated glasses to avoid paramagnetic interferences whereas real glasses may be used in NEXAFS investigations.²⁻⁶ An initial comparison of the NEXAFS and NMR results obtained from representative alkali borosilicate glasses can be made.

EXPERIMENTAL

The alkali borosilicate glasses were prepared at PNNL and characterized by standard analytical methods. The glasses are referred to by weight percent of boron as B₂O₃ (B-3 is 3 wt%). Results from boron reference compounds were used to establish the photon energy calibration and to ensure proper instrumental response. The glasses were ground to -325 mesh for all investigations. The solid state magic angle spinning (MAS) NMR measurements were made of specially-prepared glasses B-3, B-16, and B-24 at PNNL.⁷ The NEXAFS measurements at the B K edge (191 eV) of the borosilicate glasses, plus the two additional glasses S1 and S2 with unknown boron coordination that are not amenable for NMR, were performed on Beamline 7.0.1 or Beamline 9.3.2 of the Advanced Light Source at LBNL. Experiments were done under high vacuum conditions ($\sim 5 \times 10^{-9}$ Torr) with the glass powders pressed into indium. NEXAFS spectra were collected in the total electron yield (TEY) mode and on Beamline 7.0.1 in the partial fluorescence yield (PFY) mode as well. The performance characteristics of the beamline and x-ray emission spectrometer have been previously described.^{8,9} NEXAFS spectra were measured with the monochromatic x-ray beam incident at $\sim 75^\circ$ to the substrate normal.

RESULTS

The B K edge PFY spectra obtained from the glasses and normalized to the incoming photon flux are shown in Figure 1. The data were collected in the PFY mode, thereby emphasizing the bulk contribution from boron.¹⁰ Simple inspection of the overall NEXAFS signal shows that the spectra correlate nicely, as expected, to the concentration of B in the glasses. Furthermore the differences in boron spectra between the two identical glass melt compositions, one processed at 1300°C and the other at 1500°C, are clear in Figure 1. The most prominent features of the B spectra in Figure 1 are the peaks appearing just below 192 and 194 eV, respectively. An

exception is the B-3 spectrum that has much less intensity from the feature at lower energy. Examination of the spectra shows that the relative intensities of the two prominent features change with the boron content of the glasses. The peak located at 191.8 eV is well-known from NEXAFS spectroscopy of the boron K edge and is readily assigned as a transition to a π^* state.²⁻⁶

Figure 2 shows the PFY NEXAFS spectrum of hexagonal BN (h-BN), the B-24 glass, and two spectra collected from B_2O_3 with different modes of detection for comparison. The π^* transition in the glasses is indicative of structurally three coordinate boron. The higher energy peaks from the glasses resemble and occur at the same energy as the transitions observed in the PFY spectrum from three coordinate boron in B_2O_3 as shown in Figure 2. However, the peaks do not have the same linewidths and correlate to the four-coordinate boron from the reference glass materials. The TEY spectrum of B_2O_3 in Figure 2 also exhibits a π^* peak from three coordinate boron. This feature arises from near surface boron defects and are distinguished as a result the difference in surface sensitivity between the surface sensitive TEY and bulk sensitive PFY collection modes.¹⁰

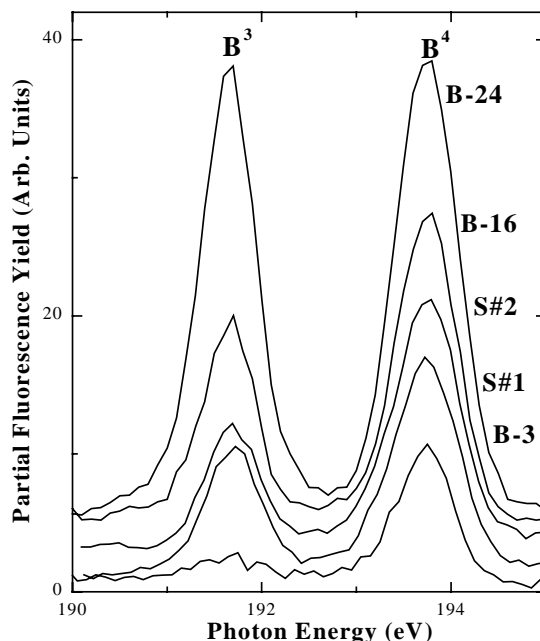


Figure 1. The raw partial fluorescence yield boron K edge NEXAFS spectra collected from the borosilicate glasses normalized to the incident photon beam current.

The relative fractions of three- to four- coordinate boron from the glasses were obtained from peak intensities of the PFY boron NEXAFS spectra. The PFY spectra were utilized for this purpose rather than the TEY spectra since this yields a bulk value comparable to the MAS-NMR results from the specially prepared glasses. The boron NEXAFS was calibrated to the MAS-NMR results. The relationship between boron coordination obtained via standards from NEXAFS to NMR are related as 2.57 ± 0.07 . Thus, knowledge of the glass compositions and some initial MAS-NMR results coupled with the boron NEXAFS peak ratios, permits the experimental determination of the amount of three coordinate boron in glasses S1 and S2. The S1 and S2 glasses are found to have approximately 82% and 84% four coordinate boron expressed in terms of atomic fraction, with the high temperature S2 glass having slightly more four coordinate boron. This may be a result of higher temperature forming four coordinate boron environments more effectively. Furthermore, these initial results suggest that the higher temperature glass lost some boron content during melt processing.

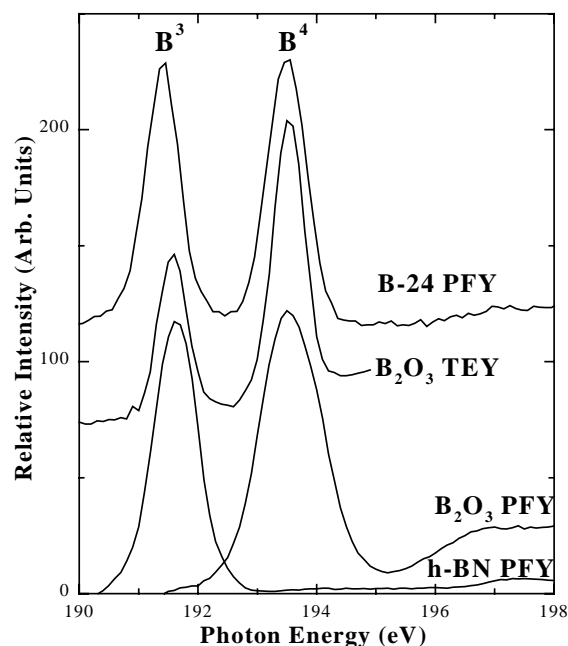


Figure 2. Boron K edge NEXAFS spectra from relevant B reference materials and the B-24 glass. The B_2O_3 spectra have been collected in two detection modes which have differing surface sensitivities. The spectra have been normalized to equivalent heights relative to the largest respective spectral feature.

CONCLUSIONS

The total NEXAFS signal at the boron K edge reflects the boron concentration in borosilicate glasses. The results show that boron K edge NEXAFS investigations can determine the amount of three coordinate versus four coordinate boron in borosilicate glasses once a suitable calibration is established. Most importantly, the results validate an experimental approach capable of ascertaining boron coordination in glasses that are not amenable to NMR methodologies. Boron K NEXAFS spectra can be obtained quickly and the interpretation of the data is straightforward once transitions are identified. The PFY and TEY modes of NEXAFS afford the opportunity to emphasize bulk or near surface region contributions to the spectra from which the information is extracted. Furthermore, there is potential to examine B coordination in glasses containing real waste, including radioactive constituents, by NEXAFS on ALS soft x-ray beamlines.

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